SAMPLING DEVICE

FIELD OF THE INVENTION

The present invention relates to a device and a method of sampling for analysis of isocyanates, aminoisocyanates, amines, isothiocyanates and carboxylic acids which are present in both gas and particle phase in an air flow.

BACKGROUND OF THE INVENTION

Polyurethane(PUR) products frequently occur in industry, in particular in manufacturing and handling polyurethane foam, elastomers, adhesives and lacquers. Polyurethane is produced by the reaction of a bifunctional isocyanate with a polyfunctional alcohol. The satisfactory technical qualities of polyurethane have resulted in a large increase of its use and application fields during the last decade. In connection with thermal decomposition of polyurethanes, however, the formation of isocyanates, aminoisocyanates and amines might occur, and extremely high contents can be found in air, e.g. when welding automobile sheet steel. Besides the known types of isocyanate, also new types of aliphatic isocyanates have been detected, in connection with e.g. heat treatment of car paint. Most of the isocyanates formed have been found to be represented by so-called low-molecular isocyanates. During short periods of time (peak exposure) particularly high isocyanate contents can be present, as is the case, for instance, when welding. Of all the dangerous substances on the limit value list, isocyanates have the lowest permissible contents. Exposure to this new type of isocyanates was previously unheard of. Isocyanates in both gas and particle phase have been detected in connection with welding, grinding and cutting of painted automobile sheet steel, and respirable particles in high contents containing isocyanates have been detected. In thermal decomposition products of painted automobile sheet steel, detection has been made of, among other things, methyl isocyanate (MIC), ethyl isocyanate (EIC), propyl isocyanate (PIC), phenyl isocyanate (PhI), 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), 2,4- and

2,6-diisocyanate toluene (TDI) and 4,4-methylene diphenyl-diisocyanate (MDI).

In thermal decomposition of phenol/formaldehyde/ urea-(FFU)-plastic, isocyanic acid and methyl isocyanate are formed. FFU plastic is used, among other things, in wood glue and as a binder in mineral wool (and bakelite), which is frequently used as insulation for ovens and furnaces in industrial and domestic use. New fields of application in which exposure to isocyanates has been detected are the soldering and processing of printed circuit boards in the electronic industry, the welding, grinding and cutting of painted sheet steel in the automobile industry and the welding of lacquered copper pipes. Isocyanates have a varying degree of toxicity to the organism depending on their chemical and physical form. As a result, the hygienic limit values have been set at an extremely low level in all countries. For the exposed individual, the degree of exposure to isocyanates varies considerably in different operations during a working day and in connection with breakdowns. Thermal decomposition products from PUR constitute a special problem, since new and completely unknown isocyanates are formed, whose toxicity has not yet been analyzed in a satisfactory manner. Furthermore, the increasingly sophisticated measuring methods have revealed exposure to isocyanates in an increasing number of operations in industry.

To sum up, there is a number of operations in numerous working areas where people are daily exposed to or at risk being exposed to isocyanates at a varying degree. Considering the ominous tendency of isocyanates to cause respiratory diseases and the fact that there are some carcinogenic substances among the thermal decomposition products of polyurethane, e.g. 2,4-diamine toluene (TDA), 4,4-methylene diamine (MDA) and MOCA, it is very important to measure in a reliable, sensitive and rapid manner any presence of isocyanates, but also other decomposition products dangerous to health, in environments where there is such a risk.

Due to the high degree of reactivity of the isocyanates with other substances containing active hydrogen, the major part of the methods utilized for measuring in air flows are based on

derivatisation in connection with the sampling step in order to protect the isocyanate group and allowing a selective determination of the isocyanates. A number of reagents and methods have been presented for the determination of isocyanates. However, there is only a limited amount of information about the reaction rate of isocyanates, and losses due to the presence of interfering substances has been reported, for instance, for 1-(2-methoxyphenyl)piperazine (2MP) and MAMA as derivatisation reagents for 2,4- and 2,6-TDI. A method recently developed by the present inventor has a number of advantages in comparison with the above-mentioned MAMA method. This new method, which is called the DBA method due to the use of di-n-butylamine as reagent, allows the analysis of several new types of isocyanates and has been suggested as an international ISO reference method. The DBA method is based on the gathering of isocyanates in impinger bottles containing DBA in toluene and having a filter which is coupled in series and situated after the impinger bottle in the flow direction. In a sampling process, DBA solution and toluene are added to an impinger bottle. Subsequently, the sample flow is calibrated. An air flow is drawn through a tube immersed in the reagent solution, and isocyanates in the air flow react with DBA in the solution. Non-reacted gaseous isocyanates which have passed the solution are drawn through a filter which is provided with a reagent and arranged in connection with the suction device. Thus on this filter isocyanates which have not reacted with the reagent solution are bound. After completed sampling, the DBA solution with bound isocyanates is conveyed to and the filter is applied to one and the same test tube for further transport to an analysis step. Impinger bottles containing 10 ml 0.01 mole DBA in toluene have been used. Deuterium-labeled isocyanate DBA derivates are added to the samples and used as internal standards. Carbamate esters are formed by adding 2 ml 5 M NaOH, 10 µl pyridine and 50 µl ethyl chloroformate to the samples. The so-called DBA method has been tested for isocyanates in connection with spray painting with two typical biuret and isocyanurate adducts, HDI, IPD, polymeric MDI, TDI and thermal decomposition products from PUR plastic. High reaction rates for

the reaction of the isocyanates with DBA have been observed, and the method is not sensitive to interfering substances. Since DBA is easy to eliminate in connection with the processing of the sample, the subsequent chromatographic determination is facilitated, which allows the use of the reagent in high contents. Before the chromatographic determination, the organic phase is separated and evaporated until it is dry. The rest is dissolved in 500 µl acetonitrile, after which the solution is injected into a liquid chromatographic (LC-mass-spectrometric (MC)) system.

Other methods used for the determination of isocyanates have a number of drawbacks. Among other things, isocyanates which are present in both gas phase and particle phase in the air flow cannot be bound to the reagent in a satisfactory manner. Isocyanates which are present on and/or in particles, such as dust, will not be completely accessible to analysis, but will be polymerized to a kind of lump. Moreover, the reaction of the reagent with isocyanates is slow and negatively affected by interference from other substances present. In addition, the minimal sampling volume is about 0.5 l air, whereas the air flow which is obtained by means of a battery-operated air pump usually amounts to about 1 l/min. Furthermore, conventional sampling devices require manual adding of solvents and reagents as well as manual dismounting to convey the reagent liquid and the filter with bound isocyanates to the final analysis test tube. Another drawback is that such a sampling device can be tampered with to obtain false results.

In view of this, there is a great demand for an improved device and an improved method for sampling isocyanates, but also other products dangerous to health, such as aminoisocyanates, amines, isothiocyanates and carboxylic acids, in a rapid, reliable, precise and tamperproof manner.

SUMMARY OF THE INVENTION

An object of the present invention is to eliminate the above-mentioned problems and provide a device and a method for improved sampling in an air flow for the analysis of isocyanates, aminoisocyanates, amines, isothiocyanates and

carboxylic acids which are present in both gas and particle phase.

According to the invention, this object is achieved by means of a device and a method, respectively, of the type mentioned by way of introduction, which have the features stated in the appended claims 1 and 20, respectively. Preferred embodiments of the sampling device and the method, respectively, are defined in the dependent claims.

According to one aspect, the present invention relates to a sampling device for the analysis of substances which are present in both gas and particle phase in an air flow.

According to another aspect, the invention relates to a method for sampling in an air flow by means of the sampling device according to the present invention.

According to a further aspect, the present invention relates to a kit containing a set of a plurality of sampling devices which contain different reagents for taking samples from different substances in an air flow, which is specified in claim 17.

According to yet another aspect, the present invention relates to a method for binding a reagent to a surface, preferably to a surface in an adsorption device 1 and a filter device 2 in the sampling device according to the present invention, which is specified in claim 18.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 schematically shows a preferred sampling device according to the present invention.

Fig. 2 schematically shows an alternative embodiment of the sampling device according to the present invention.

Fig. 3 schematically shows a further alternative embodiment of the sampling device according to the present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention is, among other things, based on a new method for the immobilization of reagents in the form of volatile primary and secondary amines on a surface. Since a number of such usable reagents are volatile, there is a great

demand for being able to immobilize or stabilize reagents on surfaces, for instance in adsorption devices of different kind, in such a manner that the volatility of the reagent is reduced at the same time as its reactivity is maintained. This problem has been solved by the present inventor by first mixing the reagent with a carboxylic acid. The carboxylic function of the mixture then provides stability to the reagent. There is an excess of primary or secondary amine in relation to the carboxylic acid. Subsequently, the mixture is contacted with the surface on which the reagent is intended to be immobilized or applied, e.g. on the inside of tubes or on particles or spheres of different kind. Due to the surface tension, the mixture is partially adsorbed physically on the surface as a coating, and the otherwise volatile reagent is retained and can pursue its activity. Any carboxylic acids can be used to contribute to the carboxylic acid function, e.g. both monovalent and polyvalent, saturated and unsaturated, but in a preferred embodiment use is made of formic acid (HCOOH), acetic acid (CH_3COOH) or propionic acid (C_2H_5COOH). Combinations of one or more different carboxylic acids are also usable.

The primary or secondary amine which constitutes the reagent can be any amine which in free form is volatile and which has a molecular weight inferior to 300. Di-n-butylamine (DBA) is particularly preferred when analyzing isocyanates and aminoisocyanates. Other examples of usable amines are other dialkylamines which meet the above restriction on molecular weight.

The expression "primary or secondary amine" which is used here also comprises an amine which, in addition to the amine group, can contain one or more other functional groups which can facilitate the immobilization and/or adsorption of and reaction with the sample substance. As examples of such amines, mention can be made of alkanolamines, e.g. ethanolamines.

The substances, from which samples are to be taken by means of the method and the sampling device according to the present invention, are primarily isocyanates, aminoisocyanates and amines, but also isothiocyanates and carboxylic acids are possible. As mentioned above, these substances are frequently

present in both gas and particle phase, which has previously made it more difficult to carry out a reliable analysis. Moreover, many of these compounds are volatile and so reactive that samples cannot be taken without chemical change thereof.

The sampling device according to the present invention comprises an adsorption device 1 which, in a preferred embodiment shown in Fig. 1, is substantially elongated, preferably tubular or hollow and cylindrical, the proportion of the length to the inner diameter being more than 5, preferably about 10. Such an adsorption tube, which is also called a "denuder", can have a length of 1 cm to 1 m and an inner diameter of 0.1 mm to 1 cm. The adsorption device 1 can be made of plastic or any other low-weight material. In the preferred embodiment with a tubular adsorption device 1, the reagent is applied or immobilized on the inner walls of the tube and mixed with carboxylic acid.

When using the sampling device, sample air containing the substance which is to be analyzed is allowed to pass through the adsorption device 1, the major content of the substance in gas phase first being adsorbed on and subsequently reacting with the reagent which is immobilized on the inside of the tube walls. However, the portion of the substance which is bound on and/or in particles is passed through the adsorption device 1 together with a small portion of the substance in gas phase which has not been adsorbed.

In another embodiment, the adsorption device 1 can consist of a bed or a plate of packed particles, e.g. of glass, silicon dioxide or plastic, on which the reagent has been immobilized in the above described manner. The dimensions of the bed are not critical, but it is preferably formed as a flat cylinder.

The sampling device according to the present invention also comprises a filter device 2, which is not critical as to dimensions, but is preferably formed as a substantially flat cylinder having an inner diameter which is greater than or equal to that of the adsorption device 1. The filter device can be of any type which provides a separation of the particle phase and the gas phase in the flow and is, for instance, made of a glass or plastic material having a pore diameter of about 0.1-20 µm,

preferably 0.3-0.5 µm, and most preferably about 0.4 µm. The filter device 2 is impregnated with immobilized reagent in the same way as the adsorption device 1. Substances in solid phase, i.e. that are present on or in particles, in the passing air flow are dissolved from the particles in the filter device 2 and react in the same way with immobilized reagent. In the case of DBA as reagent for the reaction with and binding of isocyanates, aminoisocyanates and amines, the binding reaction takes place immediately and is not affected by interfering substances in the sample.

The sampling device according to the present invention further comprises a pumping or suction device 3 which can be of any type providing the required passage of the air flow through the sampling device, but it is preferably a suction device in the form of a vacuum tube or a displacement pump, such as a hose pump, diaphragm pump, injection pump or a gear-type pump. In the preferred embodiment, this device is preferably arranged in the lower end of the sampling device, that is after the end of the filter device 2 for the discharge of the air flow. In addition, the pump or suction device 3 should not be integrated in the sampling device, but be usable more than once in contrast to a disposable sampling device. Furthermore, it should be provided with a measuring device for determining the desired amount of air that is to pass. This amount is controlled by the permissible value limit for the substance involved. The pump or suction device 3 can also be adjusted so that the passage of air is controlled in such a manner that a constant air flow is obtained during the time of sampling.

As shown in Fig. 1, in a preferred embodiment of the sampling device according to the present invention the adsorption device 1, the filter device 2 and the pump or suction device 3 are arranged in such a manner that the filter device 2 is arranged between the adsorption device 1 and the pump or suction device 3. Moreover, in this preferred embodiment the adsorption device 1 is a cylindrical adsorbent tube (denuder) comprising a reagent which has been immobilized or applied on the inside of the tube. In operation, air enters through an air inlet 6, through the adsorbent tube 1 and then through the

filter device 2 before the air flow leaves through an air outlet 7 in connection with the lower end of the filter device 2. In the most preferred embodiment, an air flow containing isocyanates, aminoisocyanates, isothiocyanates, amines and/or carboxylic acids passes through the sampling device, whose adsorbent tube 1 and filter device 2 are impregnated with di-n-butylamine (DBA). The major content of these substances in gas phase are adsorbed in and react with the reagent in the adsorption tube 1, whereas the major content of these substances in particle phase are adsorbed in and react with the reagent in the filter device 2.

However, as regards amines in the air flow, no reaction takes place with the reagent, but the amines form ion pairs with the carboxylic acids in the coating consisting of the mixture of reagent and carboxylic acids, which results in the formation of a salt.

Fig. 2 shows an alternative embodiment of the sampling device according to the present invention. The only difference in relation to the sampling device in Fig. 1 is that the adsorption device 1 and the filter device 2 are inverted, which means that as an air flow passes the major content of the substance in particle phase is first adsorbed, after which the major content of the substances in gas phase is adsorbed.

In addition, the sampling device according to the present invention comprises a reagent container 4. The reagent container 4 contains the same reagent as that immobilized in mixture with carboxylic acid in the adsorbent device 1 and the filter device 2. However, there is no carboxylic acid in the reagent container 4, and the reagent can be more or less dissolved in an organic solvent, e.g. toluene or acetonitrile, but not in alcohol. The design of the reagent container 4 is not critical, but it is preferably tubular and arranged in parallel with the adsorption tube 1. Alternatively, the reagent container 4 can be arranged concentrically with the adsorption tube 1 and thus enclose the same. Moreover, the reagent container 4 can alternatively be connected to the filter device 2. In the preferred embodiment, the reagent container 4 is, however, connected to the tubular adsorbent device 1. When a desired air flow has passed through

the sampling device according to the present invention, the air inlet 6 and the air outlet 7 are closed by means of suitable conventional closing devices. Thus a closed system is provided, in which, however, there is usually a small amount of non-adsorbed substance left in both gas phase and particle phase. To allow a complete and exact analysis of the substance which is to be analyzed, e.g. isocyanates, the reagent is let into this closed system from the reagent container 4 and reacts with the above non-reacted substance. Preferably, this takes place essentially automatically when the sampling device has been closed, but can also be carried out manually with the aid of a control means which is arranged on the outside of the sampling device. The conveyance of the reagent can, for instance, take place automatically the moment the sampling device, after sampling, is removed from its position, e.g. some kind of attachment. There is, of course, an excess of reagent in the reagent container 4 in relation to the estimated amount of non-reacted substance in the above-mentioned closed system.

The reagent container 4 can be integrated in the sampling device or detachably arranged. A switch device 5, which is situated between the reagent container 4 and the adsorption device 1 or the filter device 2, can be any conventional valve which can be opened and closed and which secures the conveyance of reagent to the adsorption device 1 and the filter device 2.

As mentioned above, the part of the sampling device which includes the adsorption device 1 and the filter device 2 can be made in one piece. Thus a spill-proof and tamperproof sampling device that is easy to handle is provided for exact measuring of the amount of a particular substance in an air flow. In addition, the sampling device can easily be kept in one's pocket, and in a manner which is advantageous in terms of security it can easily be sent on for a final analysis, e.g. by means of liquid chromatography and mass spectrometry.

If, before sampling, the sampling device is to be stored for such a long time that the stability of the reagent immobilized in the adsorption device 1 and the filter device 2 is at risk, the immobilization can instead take place immediately before the sampling by adding the mixture of reagent

and carboxylic acid to the devices 1 and 2, but this must be done early enough to allow a complete coating and immobilization to take place. This so-called activation of the sampling device can be included as an optional step in the sampling method, in particular when using unstable reagents, e.g. for measuring aldehydes. Before the activation step, the mixture can be stored in a special container which is connected to the sampling device, and the addition can be carried out by means of a switch device, e.g. a valve, which can be controlled manually or more or less automatically.

In the sampling method according to the present device, the inventive sampling device, which has been manufactured according to the above-described method for immobilization of the reagent, is placed or kept at the location where the sampling of the air flow is to take place for analysis of the specific substance. The pump or suction device 3 is set at a desired flow rate according to the permissible limit value for the substance to be analyzed.

By means of the present invention, the total amount of the substance in question in the air flow can thus be quantitatively determined in a manner which was previously not possible. If desired, the amount of the substance in gas phase can be determined separately, as well as the amount of the substance in the particle phase. However, in most cases it is above all interesting to determine at the same time the total amount of the substance in both gas and particle phase, which is achieved with the aid of the preferred embodiment of the present invention.

The sampling device according to the present invention can also be used for direct determination of the substance in question, in which case a color indicator, for instance, is brought into contact with the reacted substance in or adjacent to the sampling device.

EXAMPLE

In an experiment with an embodiment of the sampling device according to the present invention, an adsorption device (1) was used which was based on a denuder tube, whereas the filter device (2) consisted of a glass fiber filter of the type A/E

(SKC, PA, USA) having a diameter of 13 mm, a thickness of 1 mm and a pore size of 0.3 µm. The denuder tube and the filter had previously been impregnated with 100 and 50 µl, respectively, of a reagent solution, which was prepared by adding 0.5 ml pure di-n-butylamine (DBA) and 0.5 ml concentrated acetic acid to 5 ml toluene under stirring. After the addition of this reagent solution to the denuder tube and the filter, respectively, the solvent was allowed to evaporate. The filter in the sampling device is placed in a filter holder made of teflon (Millipore Swinnex 13, Milford, MA, USA).

A reagent container containing pure DBA in toluene is connected to the denuder tube in the sampling device by means of a conventional valve. In one experiment, known amounts of isocyanates, i.e. 0.3 µg phenylisocyanate, 0.3 µg hexamethylene diisocyanate and 0.4 µg toluene diisocyanate, were placed in glass tubes in front of the inlet of the sampling device. Air was passed through the sampling device by means of a conventional diaphragm pump having a flow rate of about 0.2 l/min. After 2 min, the sampling device was heated by means of a heat gun, and after a total time of sampling of 4 min the experiment was completed. DBA and toluene in the reagent container were passed through the valve into the denuder tube to react with non-reacted isocyanates in the denuder tube and the filter. The toluene which was added to the denuder tube and the filter dissolves the reaction product which is formed when the isocyanates have reacted with DBA, and therefore this reaction product is completely dissolved in the sampling device, i.e. it is not left immobilized on the inner walls of the denuder tube or on the surface of the filter. Subsequently, a predetermined amount of an internal standard in the form of deuterium-labeled isocyanates is added to the sampling device, whose inlet and outlet are then closed before transporting the sampling device to a laboratory for analysis.

Before the laboratory analysis, the sampling device was opened, and the DBA solution which was present in the same and contained the above-mentioned reaction product was conveyed to another test tube. Subsequently, the toluene was eliminated by evaporation, after which 0.5 ml acetonitrile was added. After

this, the samples were ready for analysis by liquid chromatography (LC) in connection with mass spectrometry (MS). The separation of the different isocyanate reaction products was carried out by means of LC technique and MS detection. The mass spectrometer was connected in series to an LC system. Use was made of a column of Hypersil C_{18} type.

The isocyanates were detected by monitoring $[M+1]^+$ ions for the DBA derivatives. Calibration plots were obtained from the proportions of the surfaces for the internal standard to those of the samples, and from which plots the amount of isocyanate in the sample was determined. The detection limits are about 0.2 µg per isocyanate and sample.

In the performed experiment, it was found that the isocyanates gathered in the sampling device at a yield of $100 \pm 10\%$.